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STARK AND ZEEMAN EFFECTS ON THE LOWER ELECTRONIC STATES OF s-TRIAZINE

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A detailed optical study of the lower electronic states of s-triazine in a pure crystal at 1.8°K is presented. Stark and Zeeman experiments on these states give no support to previous assignments. The experiments indicate that the lowest triplet state observed in s-triazine corresponds to either a polar A_1'' state or to an E'' state in which the orbital angular momentum is completely quenched. Optical measurements on a very weak triplet state absorption at 28930.7 cm^{-1} in s-triazine are also reported. The premilinary assignment of this line as a crystal field induced Davydov component is shown not to be inconsistent with its Zeeman effect.

1. Introduction

In a previous paper [1] we have reported the results of Stark measurements on the lowest observed triplet state in s-triazine at 28935 cm^{-1}. From these measurements we concluded that the lowest triplet state in s-triazine is of E'' symmetry. In order to arrive at a consistent interpretation of our results with known Zeeman measurements [2, 3] we concluded the triplet absorption to be of vibronic $^3E'' \otimes e'$ nature. Our Stark measurements then had to be interpreted as due to electric field induced mixing between the degenerate *vibronic* triplet states $^3E''$ and $^3A_1''$, the position of $^3A_2''$ being irrelevant.

In a forthcoming paper by Bernstein and Smalley [4] these authors also conclude from optical measurement on deutero isotopes of s-triazine that the lowest observed electronic triplet state of s-triazine is of E'' symmetry. They conclude that the state observed is of pure electronic nature. This interpretation however is inconsistent with known Zeeman measurements [2, 3]. In a recent paper by Hochstrasser [5] the whole spin–orbit coupling problem in s-triazine was discussed in detail. It was shown that experimental facts as polarization, Zeeman and Stark effects on an E'' triplet state of s-triazine can hardly be interpreted on the basis of simple spin–orbit coupling selection rules. In our previous paper [1] we had suggested that combined Stark–Zeeman measurements on the s-triazine triplet state might be helpful to solve the assignment problem.

In this paper we present the results of such experiments. We also present Stark–Zeeman measurements on a very weak triplet state in s-triazine 4.3 cm^{-1} to the *red* of the main isotope line. In addition we report the results of Stark and Zeeman measurements on both the singlet and triplet state of ring-substituted isotopes of s-triazine.

It is concluded that both the lowest singlet and triplet states, if degenerate, must correspond to states in which the orbital angular momentum is almost completely quenched. In a forthcoming publication, Bernstein and Smalley also report the use of the Stark–Zeeman effect on the main isotope lines of the singlet and triplet absorptions in s-triazine. Our results on these lines are essentially in agreement with theirs. The nature of the intriguing absorption at 28930.7 cm^{-1} is also discussed and possibilities of it being due to a Jahn–Teller component of triplet E'', vibronic triplet $^3A_2''$, s-triazine trap or Davydov component are being analyzed.

2. Experimental

For experimental details of purification and crystal growth of s-triazine we refer to an earlier paper [1]. To appreciate the results presented here one should realize that the s-triazine crystal structure is such that the three-fold (out-of-plane) axes of all molecules are parallel to one another and to the crystal c axis. At room temperature this is strictly true, at 213°K however, s-triazine undergoes a phase transition [6] and below 213°K the crystal is in fact biaxial. This situation is unfavourable since we discovered that some crystals after passing through the phase transition, completely depolarize the light. The optical quality of our crystals at 1.8°K was always checked and polarization data refer to crystals that still extinguished perfectly between crossed polarizers at 1.8°K. Some of our optical experiments (expecially those on the singlet state) were performed on a 1 meter 1704 Spex equipped with an echelle grating. The resolution of this instrument at 30014 cm^{-1} in the 17th order is about 0.05 cm^{-1}. The other experiments were performed on a $\frac{3}{4}$ meter 1702 Spex in the second order of a grating with blaze at 5000 Å. The resolution of this instrument under the conditions used is about 0.4 cm^{-1}.

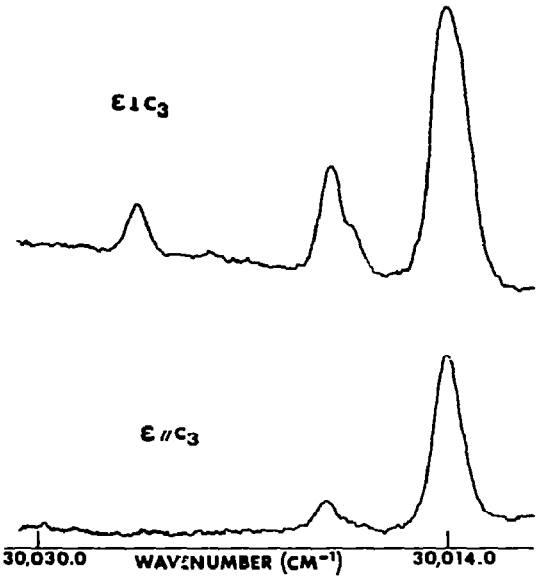

Fig. 1. Polarized absorption spectrum of a 1.5 mm thick crystal of s-triazine in the singlet region at 1.8°K. The upper spectrum was taken with the light perpendicular and the lower spectrum with the light parallel to the crystal c axis.

3. Results

3.1. Stark and Zeeman effects on the E'' singlet states near 30014 cm^{-1}

Fig. 1 shows a photoelectrically recorded polarized absorption spectrum of s-triazine near 30014 cm^{-1} at 1.8°K. The small linewidth (1.0 cm^{-1}) of the main isotope line enables us to observe weaker lines at 3.8, 4.6 and 11.9 cm^{-1}.

There are two main isotopes of s-triazine, in natural abundance of 1.2% ($^{15}NC_3N_2H_3$) and 3.3% ($^{13}CC_2N_3H_3$), that have to be considered. Fig. 2 shows the effect of an electric field applied perpendicularly to c on the main isotope and its substructure. We observe a linear Stark splitting for all lines (the weak line at 3.8 cm^{-1} could not be observed in this experiment) and this is shown in the inset of fig. 2. This fact means that the first two lines at 3.8 and 4.6

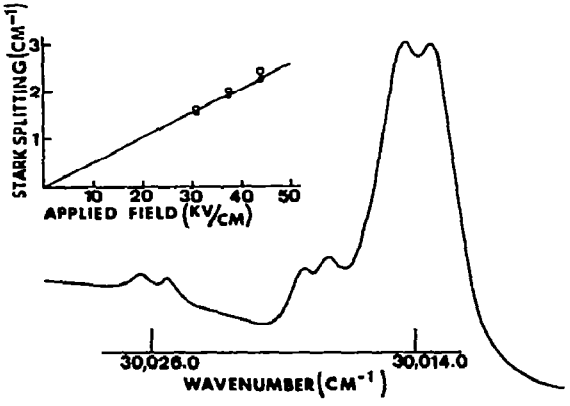

Fig. 2. Electric field effect on s-triazine and its isotopes in the singlet region. The electric field was 21 kV/cm and applied perpendicular to the crystal c axis. The inset shows the linearity of the Stark splitting versus applied electric field. The open circles refer to splittings of $C_3N_3H_3$ and $^{13}CC_2N_3H_3$ absorptions and the solid dots refer to the splitting of the $^{13}C^{13}CCN_3H_3$ absorption line (see also table 1).

Table 1
Line positions and interpretation of the isotopic structure near the lowest observed singlet and triplet states in s-triazine

Isotope	Position (cm^{-1})± 0.2	Position (cm^{-1})± 0.2
	singlet	triplet
$C_3N_3H_3$	30014.0	28935.0
$^{15}NC_3N_2H_3$	30017.8	28939.5
$^{13}CC_2N_3H_3$	30018.6	28940.4
$^{13}C^{13}CCN_3H_3$	30025.9	28948.8

cm^{-1} cannot correspond to an electronic splitting of a ring-substituted isotope of s-triazine. Intensity considerations then favour assingnments of these lines as made in table 1. The appearance of a line at 11.9 cm^{-1} to the blue of the main isotope, which we have interpreted as $^{13}C^{13}C\,CN_3H_3$ is not inconsistent with observations made, e.g., near the lowest triplet state of *p*-dichlorobenzene [7]. Our conclusion therefore is that isotopic ring substitution in s-triazine is not able to lift the degeneracy of the E″ singlet state.

We have also examined the absorption of the crystal shown in fig. 1 in a magnetic field of 73.5 kG parallel to the crystal *c* axis (molecular three-fold axis).

We have not been able to observe any splitting or broadening of either the main line at 30014 cm^{-1} (linewidth 1.0 cm^{-1}) or any of the isotopic impurity lines. This result contradicts the reported splitting of the main line at 30014 cm^{-1} with a magnetic field along the three-fold axis by Hochstrasser and Zewail [8]. In fact this result as reported by these authors was one of the most compelling reasons to accept the orbital degeneracy of the 30014 cm^{-1} singlet absorption.

Our Zeeman measurements indicate that the spectroscopic *g*-factor of this state could not be greater than 0.03.

As it stands now the reported [9] mixed magnetic and electric dipole absorption characteristics of this state are the only indication of its orbital degeneracy.

3.2. The triplet states near 28935 cm^{-1} and their Stark–Zeeman effects

Fig. 3 shows the photo-electrically recorded absorption spectrum of an s-triazine crystal in the lowest

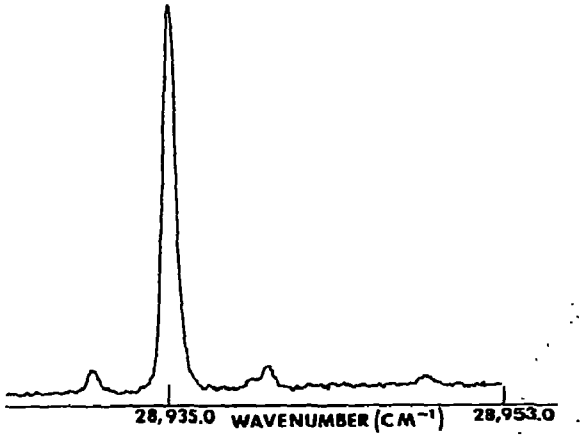

Fig. 3. Unpolarized absorption spectrum of s-triazine in the triplet region at 1.8°K. The crystal thickness was 10 mm.

triplet state region. This crystal extinguished completely between crossed polarizers and we find indeed that 84% of the light is absorbed with the electric vector parallel to the out-of-plane axis. The linewidths observed in this crystal were 0.7 cm^{-1}. Isotopic structure similar to that observed for the lowest singlet state is found at 4.5, 5.4 and 13.8 cm^{-1} from the main line at 28935 cm^{-1}.

The interpretation of these lines should be analogous to that given for the singlet state region and can be found in table 1. We note however that the isotopic trap depths near the triplet state all are found to be larger than those near the singlet state. If the singlet and triplet states correspond to narrow exciton bands as believed [10] then we find that vibrational frequencies are less reduced in the lowest triplet than in the lowest excited singlet state upon isotopic ring substitution. This could be another manifestation of the difference in configuration interaction [1] among the E″ states [$e''(\pi^*) \leftarrow e'(n)$ and $e''(\pi^*) \leftarrow a_1'(n)$] forming the lowest triplet and singlet E″ states.

A new feature unprecedented in the singlet absorption spectrum is a line observed at 4.3 cm^{-1} to the red of the main isotope absorption. The fact that this line is *not* observed in the singlet state region in crystals of much higher optical density for the main line makes the explantation of it as in s-triazine-trap absorption, unlikely.

In order to study further the nature of this and the other triplet absorption lines near 28935 cm^{-1} we

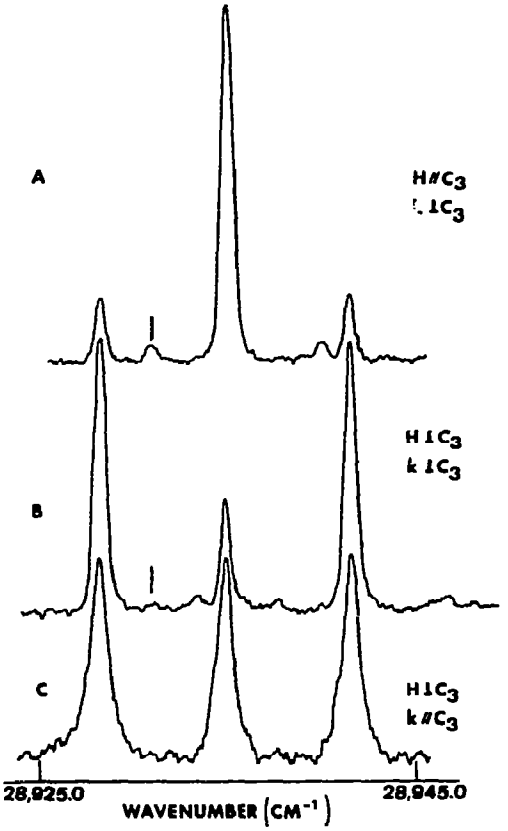

Fig. 4. Unpolarized absorption spectrum of s-triazine in the triplet region in a magnetic field of 73.5 kG at 1.8°K (k is the propagation vector). The position of the absorption at −4.3 cm^{-1} from the main isotope in the field is indicated by bars.

have examined these absorptions in high magnetic and electric fields. The results of our Zeeman experiments in a magnetic field of 73.5 kG are shown in fig. 4. The first two spectra, with respect to the main isotope line are essentially in agreement with earlier measurements [2, 3] and yield an isotropic g-value of 1.95 ± 0.02. The same g-tensor is also found for the ^{13}C-s-triazine absorption at 28940.4 cm^{-1}.

The spectrum shown in fig. 4c has not been reported before and the total integrated absorption intensity of the Zeeman components for this orientation is only 0.09. The interesting feature of this measurement is the fact that in this orientation the polarization vector of the light only selects in-plane intensity sources. This experiment clearly shows that the in-

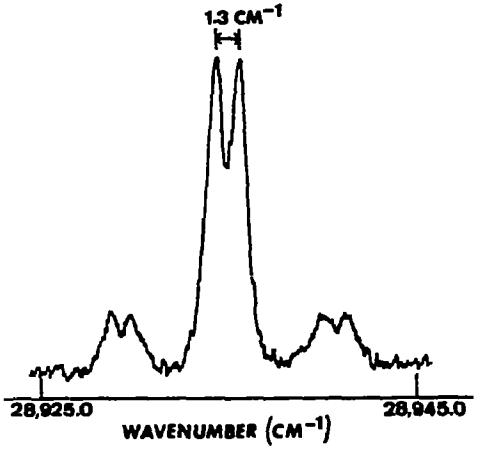

Fig. 5. Stark–Zeeman effect on the 28935 cm^{-1} triplet state of s-triazine at 1.8°K. The magnetic field of 61.2 kG is parallel to, and the electric field of 35 kV/cm is perpendicular to, the crystal c axis.

plane spin substates are mainly responsible for spin–orbit coupling into the $\pi\pi^*$ singlet manifold. We further observed (fig. 4a, b) that the weak absorption at 28930.7 cm^{-1} (OD ≈ 0.02 per cm for the 0.7 cm^{-1} wide line) exhibited the same kind of Zeeman intensity pattern as the main isotope line. This thus proves that this state also is a triplet state with the a_2' (R_z) spin substate being the active one. Its g-factor ($g \perp c$) was also found to be 1.95 ± 0.02.

We thus conclude that this line is also due to an s-triazine species. The overall conclusion from the Zeeman experiments is that, if the triplet states observed are degenerate, they correspond to states in which the orbital angular momentum is almost completely quenched.

To further explore the possibilities of electric field induced mixing of the Zeeman components of the main line with other states in this region, we have performed Stark–Zeeman measurements on the main isotope line for the magnetic field parallel and perpendicular to the crystal c axis. In fig. 5 the results of one of these experiments are shown. In every case we found that our Stark–Zeeman spectra are just combinations of individual Stark and Zeeman spectra. There is no indication of electric field induced mixing of the spin substates with other states in the region covered by the magnetic field perturbation.

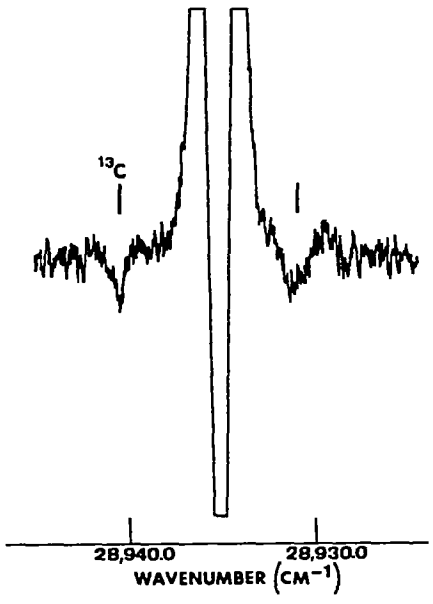

Fig. 6. Phase sensitive detected Stark effect on the triplet state absorptions near 28935 cm^{-1} at 1.8°K. E_{dc} = 32 kV/cm, E_{ac} = 43 kV/cm (top–top). The zero-field positions of the line at –4.3 cm^{-1} to the main isotope and ^{13}C-s-triazine are indicated by bars.

Finally in fig. 6 we show the result of a Stark experiment on the triplet state absorptions. Herein we see that both the absorptions at –4.3 and 5.4 cm^{-1} to the main isotope are split in an electric field and essentially yield the same Stark effect. This just proves that the triplet state at –4.3 cm^{-1} is also polar and strengthens our belief that this absorption is due to the same species as that responsible for the absorption at 28935 cm^{-1}.

4. Discussion

Our experiments have shown that the assignment of the lowest observed singlet state in s-triazine at 30014 cm^{-1} as E″ on the basis of its Zeeman effect is not warranted. Stark effect measurements on the ring-substituted isotopes of s-triazine also did not indicate any expected zero field splitting of an E″ state in these s-triazine isotopes. These experiments thus seem to suggest that one deals here with a non-degenerate singlet state of s-triazine, that is polar in the low-temperature crystalform. Polarization and Stark effect measurements on the main isotope line at 30014 cm^{-1} though seem to be a firm indication of its electronically degenerate nature. The absence of a magnetic field effect can then be explained as a quenching of the orbital angular momentum if this state in the crystal. At this point it seems inappropriate to draw any firm conclusion with regard to the electronic symmetry of the lowest singlet state in s-triazine. We feel that magnetic circular dichroism measurements on this singlet state might be very useful and give a better insight in the magnetic properties of this state.

The main conclusion from our Stark–Zeeman experiments on the triplet state at 28935.0 cm^{-1} is that we have not obtained any indication of its proposed [1, 4] orbital degeneracy. The effects observed can all be explained if the state is a *polar* $^3A_1''$ state. Again such a polarity of an s-triazine excited state is difficult to interpret.

As mentioned before, one of the most intriguing features to explain in the triplet state region is the presence of a very weak triplet state at 28930.7 cm^{-1}.

Several possibilities for *this* absorption will now be analyzed. (1) The state observed is the vibronic triplet state $^3A_2''$. In our previous paper we suggested that the triplet state at 28935.0 cm^{-1} is due to the degenerate vibronic components $^3E''$ and $^3A_1''$, the position of the vibronic $^3A_2''$ state being irrelevant. The observed polarity of the weak absorption, as shown in fig. 6, is inconsistent with an assignment of this state as $^3A_2''$. (2) The weak triplet state is one of the components of triplet E″, the other component being the stronger triplet absorption at 28935.0 cm^{-1}. The splitting observed (4.3 cm^{-1}) is then induced by the crystal field in the low-temperature crystal form of s-triazaine. Although we cannot disregard this possibility, it is hard to understand why the intensity imbalance among the components is as drastic as observed. We also have failed to observe any second-order Stark shift (up to 0.1 cm^{-1}) of either component. Such a shift would be expected in this case. (3) We deal in this absorption with an s-triazine trap. In principle some of the high-temperature crystal form of s-triazine could be present in the low-temperature form, giving rise to the weak absorption at 28930.7 cm^{-1}. We feel that this interpretation is inconsistent with the fact that a similarly weak absorption is absent in the singlet

state region, (4) The weak absorption at 28930.7 cm^{-1} is a Davydov component of the s-triazine triplet state, the other exciton component being the strong line at 28935.0 cm^{-1}: The observed intensity ratio (40 ± 5 : 1) is in reasonable agreement with the calculated [6] ratio of (49 : 1) in the low-temperature monoclinic crystal form. One predicts [11] for such an exciton component that in a magnetic field parallel to the crystal c axis and using unpolarized light the central line ($m_S = 0$) to be reduced by 50% with respect to the zero-field situation. Our preliminary Zeeman experiments on the weak line are not inconsistent with such an analysis. In this calculation we have assumed that the only active spin state is a_2' (R_z). Our polarized absorption spectra show that 84% of the total triplet absorption intensity is provided by this spin substate (see also fig. 4).

We thus have shown that there are several alternative explanations for the weak absorption at 28930.7 cm^{-1}. At this moment we are in favour of the last explanation proposed. Here in a natural way the intensity imbalance is explained and the absence of a similar absorption in the singlet region does not weaken the assignment. Polarized Zeeman absorption spectra will definitely settle the present problem. We are presently engaged in producing a much better signal-to-noise ratio for the weak absorption (OD = 0.02 per cm for the 0.7 cm^{-1} wide line) to be able to perform such an experiment.

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References

[1] D.A. Wiersma, Chem. Phys. Letters 16 (1972) 517.
[2] R.M. Hochstrasser and T.S. Lin, Symp. Faraday Soc. 3 (1969) 100.
[3] R.M. Hochstrasser and A.H. Zewail, J. Chem. Phys. 55 (1971) 5291.
[4] E.R. Bernstein and R.E. Smalley, J. Chem. Phys. 58 (1973), to be published.
[5] R.M. Hochstrasser, Chem. Phys. Letters 17 (1972) 1.
[6] P. Coppens and T.M. Sabine, Mol. Cryst. 3 (1968) 507.
[7] G. Gastro and R.M. Hochstrasser, J. Chem. Phys. 46 (1967) 3617.
[8] R.M. Hochstrasser and A.H. Zewail, Chem. Phys. Letters 11 (1971) 157.
[9] R.M. Hochstrasser, T.S. Lin and A.H. Zewail, J. Chem. Phys. 56 (1972) 637.
[10] G. Fischer, J. Chem. Phys. 57 (1972) 2646.
[11] R.M. Hochstrasser, J. Chem. Phys. 47 (1967) 1015.